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Numerical Investigations of the Glass Transition and Glassy State of Structural Glasses and Spin Glasses

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Monte Carlo and molecular dynamics simulations of various models of glass–forming systems are described, aiming at a better understanding of the amorphous state of matter, and to clarify how a liquid transforms into a glass. Our studies range from chemically realistic models of silica (SiO_2) and SiO_2–Na_2O glasses over simpler models like binary Lennard–Jones fluids to abstract spin models such as the so–called Potts glass. The motivation to study such models will be briefly addressed, and the reason will be explained why massive computational efforts on large–scale supercomputer facilities are crucial to make progress in this field. Results will be presented on bulk properties as well as on systems confined to small droplets or thin films.

1 Introduction

While within solid state physics the properties of crystalline materials are rather well understood, the amorphous state of matter still poses significant challenges: in a crystal the atoms form a periodic lattice, while in a glassy material the geometric arrangement of the atoms exhibits only order on short length scales, but no (known) long range order. Thus, while single crystals have a regular external shape with facets meeting under particular angles, glasses have no particular shape, and that is why these materials are called "amorphous". While in a crystal lattice different directions are usually not equivalent, and physical properties hence exhibit more or less anisotropy, glasses are completely isotropic, just like fluids. This isotropy (and also their homogeneity on mesoscopic and macroscopic scales) is, e.g., very desirable for many optical applications, such as lenses or prisms (e.g., obviously it would be difficult to make eyeglasses from crystals because of their birefringence), although in the following we will not discuss these issues further.

If one analyzes the structure of glass on an atomistic scale (by performing scattering experiments of X–rays or neutrons), one obtains a picture very similar to the corresponding liquid. Therefore it is sometimes said that a glass is a "frozen liquid", where atoms are no longer allowed to move over larger distances. But what mechanism prevents this motion? And already in the liquid phase one finds a dramatic slowing down if the liquid is cooled down towards the temperature where the glass transition occurs. As an example, Fig. 1 shows the diffusion constants of silicon (Si) and oxygen (O) atoms in molten silica[1]: one observes a decrease of these diffusion constants D (and this corresponds simply to an increase of the structural relaxation times, $\tau \propto D^{-1}$) over about 15 decades! Over most of this range, the structure of the fluid changes very little (at least as far as properties as

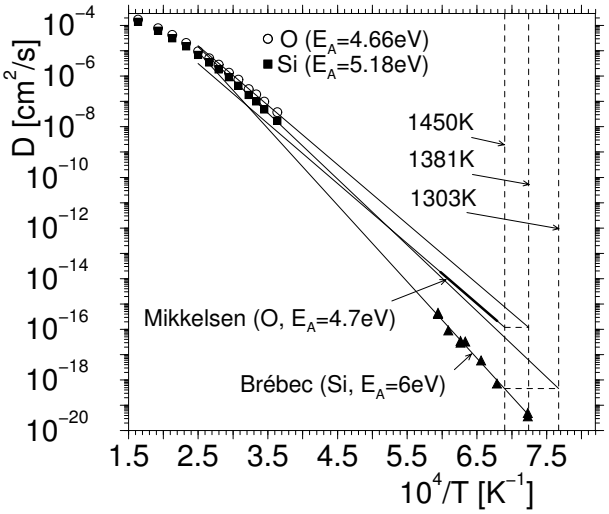

Figure 1. Semilog plot of the self–diffusion constant D of silicon atoms (filled squares) and oxygen atoms (open circles) in molten SiO_2 plotted vs. inverse temperature, including molecular dynamics results (upper left part) and experimental data (lower right part). The thin straight lines indicate simple Arrhenius behavior, $D \propto \exp\left[-E_{\rm A}/(k_B T)\right]$, with various values of the activation energies E_A. The vertical broken lines indicate the experimental glass transition temperature, $T_{\rm g} = 1450$ K, and the ones estimated from the Arrhenius laws of the diffusion constants of our simulation ($T_{\rm g} = 1303$ K for Si and $T_{\rm g} = 1381$ K for O). From Horbach and Kob[1].

pair correlation functions between atoms, as accessible via scattering experiments, are concerned), and hence this dramatic slowing down is very puzzling. Fig. 1 also illustrates that it is very difficult to address this problem by means of computer simulations: in a liquid, local motions are rather fast (atomic vibration times are of the order of 10^{-13} sec), while near the glass transition τ, the time scale for the structural relaxation, is of the order of 10^2 sec. (If the fluid is cooled below the glass transition temperature $T_{\rm g}$, it falls out of equilibrium and stays more or less frozen as a solid, i.e. τ diverges). A molecular dynamics simulation amounts to solve numerically Newton's equations of motion of classical mechanics for all the interacting atoms in the model system. (Typically one uses a simulation box containing a few thousand atoms and applies periodic boundary conditions to make the system quasi–infinite.) Since the time step δt of the integration routine must be distinctly smaller than the shortest characteristic time of the system, 10^{-13} sec, for the simulation data in Fig. 1 a time step $\delta t = 1.6 \cdot 10^{-15}$ sec had to be used. Thus one has to make many of these steps if one wants to reach mesoscopic time scales. Furthermore also the calculation of the forces with which the atoms interact needs a lot of computer time due to the long range of the Coulomb interactions between the ions (these forces cannot be truncated and therefore necessitate the use of the so–called Ewald summation technique). Therefore the data of Fig. 1, where one needed to extend the simulation to $2 \cdot 10^{-8}$ sec, i.e. $1.2 \cdot 10^7$ time steps, could only be generated on a high performance supercomputer (the CRAY–T3E of the NIC was used with parallelization of the calculation of the forces). Despite this effort it is obvious that there is a gap between the temperature range at which simulations can be done *in equilibrium* and the temperature scale accessible to experiments, and at the present

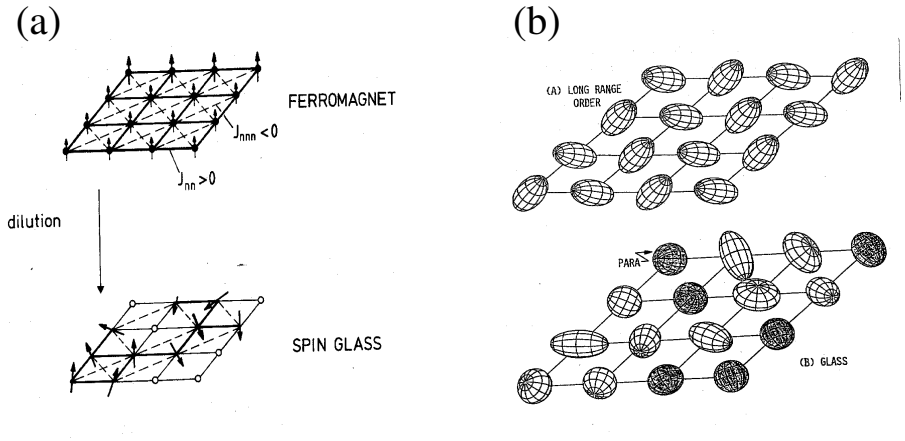

Figure 2. Schematic explanation how quenched disorder by random dilution leads, (a) from a ferromagnet to a spin glass or, (b) from a molecular crystal to a quadrupolar glass. The ferromagnet corresponds to Europium Sulfide, showing only one plane of the face centered cubic lattice, where magnetic exchange interactions occur essentially only between nearest (J_{nn}) and next nearest ($J_{nnn} \approx -J_{nn}/2$) neighbors. Random dilution with non–magnetic Strontium leads to the spin glass $Eu_xSr_{1-x}S$ (if the concentration x of Europium lies in the range $0.13 < x < 0.5$). Arrows indicate the orientation of the magnetic moments in each case. The long range ordered molecular crystal refers to ortho–hydrogen, showing again one lattice plane of the crystal only. Ellipsoids indicate the orientation of the quadrupole moments of the hydrogen molecules. Dilution with para hydrogen, which has no quadrupole moment, yields a quadrupolar glass.

time this gap can be bridged only by extrapolation. Nevertheless, the simulations do already now allow to reach various conclusions which are very useful for the interpretation of experimental results and for testing the validity of analytical theories, as we shall see (Sec. 2).

While in SiO_2 really small relaxation times (small means here $\tau \approx 10^{-13}$–10^{-10} sec) are only reached at extremely high temperatures, that are not accessible to experiment as Fig. 1 shows, in the so–called "fragile glasses" τ decreases from $\tau \approx 10^2$ sec at $T_{\rm g}$ to small values very rapidly, in a temperature interval of the order of 100 K, and hence are well accessible to experiment. These fragile glassformers typically are materials formed from organic molecules, including polymers which are the basis of the ubiquitous plastics materials. Due to the complicated chemical structure of all these molecules, chemically realistic models of these systems pose similar difficulties to simulation as in the case of SiO_2. But experiment shows that all these fragile glassformers behave qualitatively very similar. There is a remarkable degree of universality, irrespective of the differences in the chemical structure. This fact suggests to simulate a simpler model, a fluid consisting of two types of atoms denoted symbolically as A and B, interacting with short range pair potentials $U_{\rm AA}(r)$, $U_{\rm AB}(r)$, and $U_{\rm BB}(r)$. These potentials are "freely invented" and chosen such that neither crystallization nor phase separation occurs, at least not on any time scales relevant for simulation. We shall present a few results for this model that have clarified important theoretical questions in Sec. 3.

But also in this model it is not possible to equilibrate the system in the vicinity of $T_{\rm g}$ or at even lower temperatures. In order to test issues pertaining to such low temperatures,

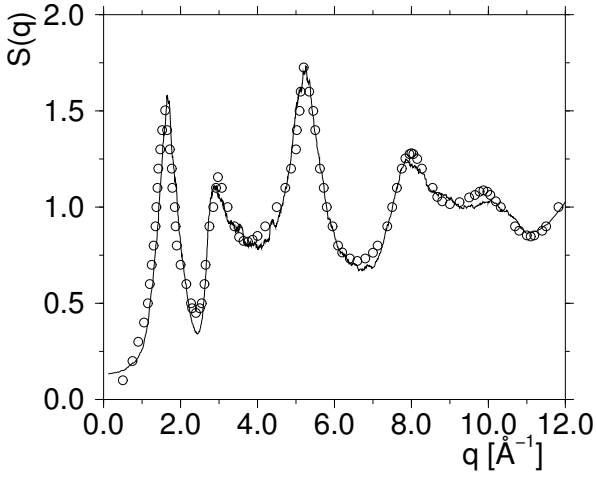

Figure 3. Static structure factor of quartz glass (SiO_2) at room temperature ($T = 300$ K) plotted vs. wavenumber q (q is related to the scattering angle θ as $q = (4\pi/\lambda)\sin\theta$, λ being the wavelength of the radiation used for the scattering experiment). The full curve is the molecular dynamics simulation of Ref.[1], using the measured neutron scattering lengths of Si and O atoms, and the circles are a neutron scattering experiment[5].

one has to restrict oneself to even more abstract models, that in a strict sense do not really represent amorphous materials, but rather crystalline solids in which other degrees of freedom exhibit glass–like relaxation. Examples for such systems are the so–called "spin glasses" and "orientational glasses"[2,3]. Spin glasses are created by random dilution of a ferromagnet with competing interactions (Fig. 2): disorder plus frustration cause the spins to freeze in random directions[2]. Similarly, random dilution of molecular crystals creates orientational glasses: electric dipole or quadrupole moments freeze in random orientations (Fig. 2). We shall also present some very interesting simulation results about such models (Sec. 4), before we summarize and conclude (Sec. 5).

2 Simulation of Molten Quartz and Sodium Silicate Glasses

SiO_2 is suitable for a molecular dynamics simulation, since accurate (pairwise) potentials could be extracted from quantum chemistry methods[4] that faithfully simulate the covalent bonding in this material, and reproduce well many known properties of crystalline SiO_2. While we can equilibrate SiO_2 only at rather high temperatures (e.g. $T = 2750$ K), cooling such melts down to $T = 300$ K with the slowest rates acceptable for a simulation (still as high as 10^{12} K/sec!) at constant density yields a structure factor $S(q)$ in very good agreement with scattering experiments (Fig. 3). Here $S(q)$ represents the intensity of the radiation observed with a momentum transfer $\hbar q$. In the comparison of Fig. 3 no adjustable parameters whatever enter, and thus this comparison shows that our simulation can *reproduce experiment*. But more importantly, the simulations can *go beyond experiment* in various ways: e.g., for the mixture Na_2O–SiO_2 we have measured all 6 partial structure factors $S_{\alpha\beta}(q)$ ($\alpha, \beta = \mathrm{Na}, \mathrm{O}, \mathrm{Si}$), which are not accessible experimentally[6], but are needed to develop a detailed picture of the atomistic structure. Another relevant infor-

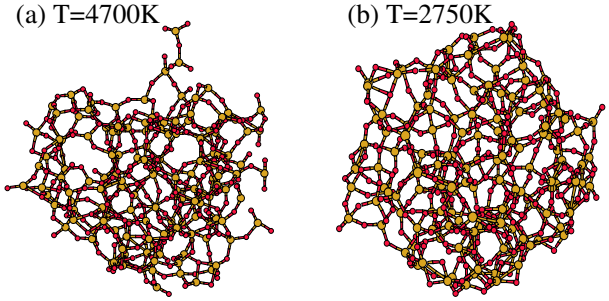

Figure 4. Snapshot of a SiO_2 cluster with 432 ions at two different temperatures. The red and yellow spheres correspond to silicon and oxygen atoms. Covalent bonds between them are drawn as little sticks if their distance does not exceed 2.3 Å. From Roder *et al.*[7].

mation is nature of the local ordering at free surfaces of molten (or frozen) SiO_2 against vacuum. We can study this problem by simulating a finite cluster with a free surface (Fig. 4). Note that in the ideal random SiO_2 network there are chemical rules concerning the nearest neighbor coordination of each atom: each Si atom wants to be linked by covalent bonds to 4 oxygen atoms, and in turn each oxygen atom wants to have two Si neighbors. Thus, the glass structure can be viewed as a network of distorted tetrahedra (with Si in the center of the tetrahedra, oxygen atoms at their corners), linked together at the tetrahedra corners with almost random angles. In such a structure, there are almost no "dangling bonds", i.e. oxygen atoms that have a single silicon neighbor. However, while such a structure seems natural in the bulk, it is not clear how this structure will change in the vicinity of a free surface against vacuum (we disregard here the problem encountered in practice that the vacuum is not perfect and water molecules or other molecules may supply ions to saturate the dangling bonds at the surface). The snapshots (Fig. 4) show that for very high temperatures indeed many "dangling bonds" are found, while for the still rather high temperature $T = 2750$ K the dangling bonds are already rather scarce, and a closer analysis shows that the network adjusts by an enhanced density of oxygen atoms in the surface region, to maintain a perfect coordination.

Note that the coordination is not truly perfect in the bulk phase of molten SiO_2: there does occur a small fraction of Si atoms with five oxygen atoms as nearest neighbors and a corresponding fraction with three neighbors[1]. The motion of these coordination defects and associated breaking of covalent bonds is in fact responsible, that a network as shown in Fig. 4 is not just an elastic solid but still a fluid! In fact, the self–diffusion constant of oxygen atoms is inversely proportional to the average "lifetime" of the covalent Si–O bonds[1].

3 A Simplified Model of a Glass–Forming Fluid: The Binary Lennard–Jones Mixture

The computer simulation of SiO_2 and silicate melts is very expensive regarding computer time because of the long range of the Coulomb interaction between the ions (the potential energy decays with distance r as $1/r$). In molecular fluids like ortho-terphenyl or

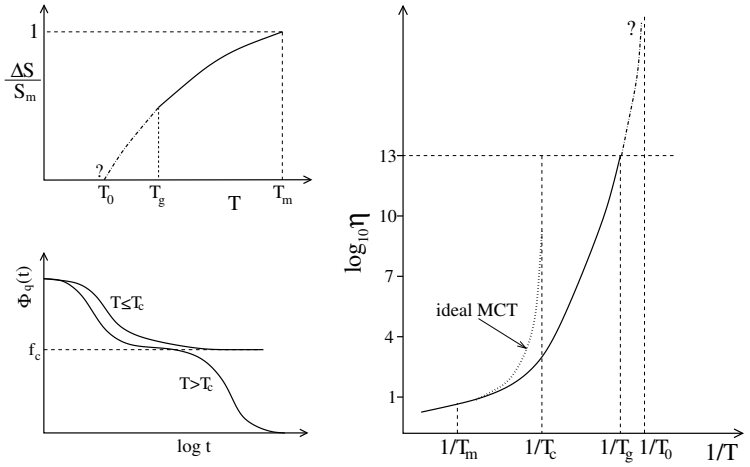

Figure 5. Schematic plot of the viscosity $\eta(T)$ of a fluid vs. inverse temperature $1/T$. Characteristic temperatures are indicated: melting temperature T_m, critical temperature T_c of mode coupling theory (MCT), glass transition temperature $T_{\rm g}$ — defined empirically via $\eta(T = T_{\rm g}) = 10^{13}$ Poise — and the Vogel–Fulcher temperature T_0, respectively. The lower left part shows the schematic behavior of the Fourier transform of density correlations $\Phi_q(t)$ according to idealized MCT: for $T > T_c$ this correlator decays to zero as a function of time t in two steps (β relaxation, α relaxation). For $T < T_c$ only the first step remains, the system is frozen at a plateau value $f_c(q)$, the so–called "non–ergodicity parameter". The upper left part shows the normalized entropy difference $\Delta S/S_m$ (S_m is the entropy difference at T_m) between fluid and crystal as a function of temperature: often these data are compatible with a linear extrapolation according to which ΔS vanishes at T_0, giving rise to the so–called "Kauzmann paradox"[9–11].

in polymer melts, intermolecular forces are much shorter ranged, but the chemical structure of the molecules itself presents a complication. Qualitatively, however, one still can capture the essential features of the glass transition even if one disregards this complication and assumes spherical particles interacting with simple Lennard–Jones (LJ) potentials, $V_{\alpha\beta} = \epsilon_{\alpha\beta}\left[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}\right]$, where the parameters $\epsilon_{\alpha\beta}$, $\sigma_{\alpha\beta}$ describe the strength and the range of this pairwise interaction between particles of type α and β. Here we have anticipated that it is necessary to work with a binary mixture of two kind of particles A and B (so three types of pairs $\alpha\beta$ = AA, AB, and BB occur): a single component Lennard–Jones fluid would be a good model of a rare gas fluid, and rare gases crystallize easily, so they are no glassformers! However, tuning the parameters $\{\epsilon_{\alpha\beta}, \sigma_{\alpha\beta}\}$ for the binary mixture suitably, an excellent model for a glass–forming fluid is obtained[8], well suited for a test of various theoretical concepts about the glass transition.

Some of these concepts are sketched in Fig. 5: According to the entropy theory of the glass transition[9,10], glassy freezing is caused by the vanishing of the configurational entropy of the supercooled fluid at the temperature T_0 ($< T_{\rm g}$), which should lead to a divergence of the viscosity according to the Vogel–Fulcher law, $\log \eta(T) \propto (T - T_0)^{-1}$. Although experimental data for the entropy[11] and viscosity[12] are often compatible with such an interpretation, it is very speculative because always T_0 is distinctly lower than $T_{\rm g}$ (e.g. $T_{\rm g} - T_0 \approx 50$ K), and the mathematical approximations involved[9,10] are rather crude and questionable.

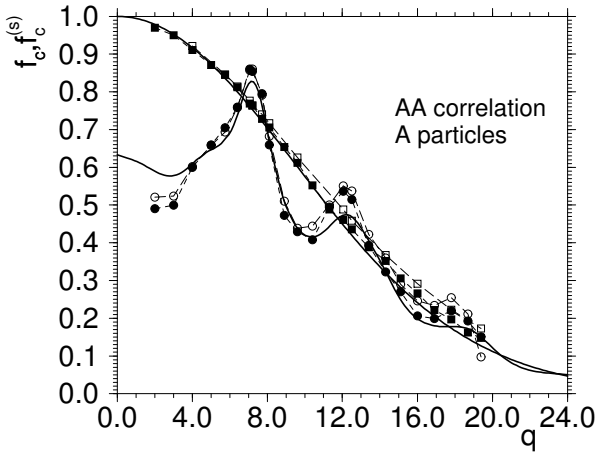

Figure 6. Wave–vector dependence of the nonergodicity parameter for the coherent (circles) and incoherent (squares) intermediate scattering function $\Phi_q(t)$ of a binary LJ mixture (80% A, 20% B). Filled and closed symbols refer to two different types of computer simulations, namely stochastic dynamics and Newtonian dynamics, respectively. The two solid lines are the predictions of idealized MCT for this system[14].

A complementary concept is the mode coupling theory (MCT) of the glass transition[13], which tries to describe the dynamics of the supercooled fluid on the atomic scale. I.e., it focuses on the time–displaced density–density correlation function $\phi_q(t)$ for wave-vector q (Fig. 5). According to the idealized version of MCT, $\phi_q(t)$ decays quickly to zero at high temperatures, while there exists a critical temperature T_c ($T_c > T_{\rm g}$) where the behavior changes drastically: a plateau develops in $\phi_q(t)$ for $T \geq T_c$, and the "lifetime" of this plateau diverges as $T \to T_c$. For $T < T_c$, the system gets "stuck", $\phi_q(t)$ does no longer decay to zero any more, but relaxes only to the "nonergodicity parameter" $f_c(q)$. The physical explanation for this behavior is the "cage effect": in a dense fluid, the motion of each atom is hindered by the atoms in its neighborhood, and as the temperature gets lower, it is no longer possible for an atom to escape from this "cage". However, this theory would imply that the structural relaxation time (and hence the viscosity) would diverge according to a power law as $T \to T_c$ which disagrees with experiment. In the more refined "extended MCT" this divergence at T_c is replaced by a smooth crossover from a power law to a simple Arrhenius behavior, and this is perhaps compatible with most experiments.

Now the "time window" corresponding to $10^{-1} \leq \eta(T) \leq 10^2$ Poise, where idealized MCT should work, is well accessible to molecular dynamics simulations of simple fluids as the binary LJ mixture introduced above. Thus, a stringent test of this theory could indeed be performed (Fig. 6)[14]. Since the static structure factor measured in the simulation is the only input needed for the theory, one again notes excellent agreement without adjusting any fit parameters. A prediction of the theory, namely that $f_c(q)$ is independent of the nature of the underlying microscopic dynamics could be tested directly by comparing a stochastic dynamics simulation (where a random force and a damping force is added to the equations of motion) to the standard (Newtonian) molecular dynamics simulation[14].

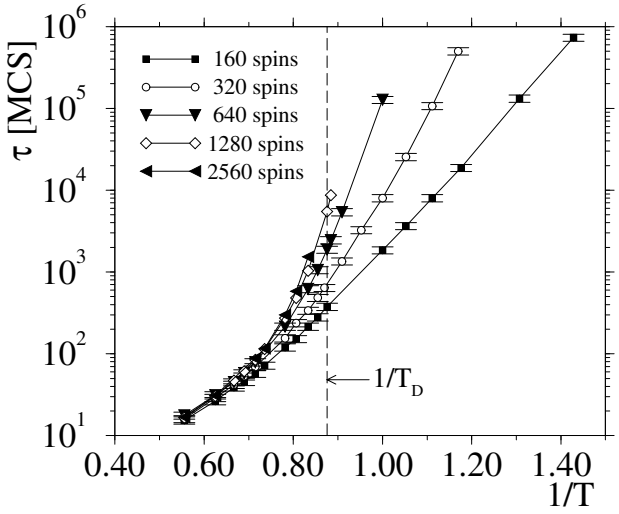

Figure 7. Relaxation time τ (in units of Monte Carlo steps per spin) of the $p = 10$ state Potts glass with random mean field interaction plotted vs. inverse temperature, for different system sizes. The vertical broken line indicates the dynamical transition present in the thermodynamic limit. From Brangian *et al.*[21]

This model is also suitable to address a question that currently finds much attention[15], namely the question how a confinement of the liquid in cylindrical pores or in slit pores affects the glass transition. Experimentally this problem is very difficult, since one does not know precisely the interactions between the liquid and the walls of the pore and also the density of the fluid in the pore is hard to control. Simulations have a distinct advantage here: we can create a pore[16] by introducing a virtual (cylindrical) wall in a bulk system, and freezing all particles outside of this wall at their positions at this instant of time. In this way, the interactions between particles in the fluid, and the particle–wall interactions are very well controlled, the geometric structure of the confined fluid remains almost unaffected, and the effect of confinement on the dynamics can be nicely analyzed! This is an example that shows that with simulations one can prepare more ideal conditions for an "experiment" than it would be possible in reality, and thus precise conclusions can be drawn, while in experiments it is rather ambiguous how the different effects can be disentangled[15]. In this way it was possible to demonstrate that near the confining wall the cage effect is enhanced due to the atomic roughness of this wall[16], i.e. the relaxation slows down. As one approaches the glass transition, the length scale over which the atoms are affected by this confining wall grows[17].

4 The 10–State Mean–Field Potts Glass: An Abstract Model for the Structural Glass Transition?

For the model of SiO_2 in Sec. 2, the lowest temperature that could be simulated in thermal equilibrium was $T = 2750$ K, while the experimental glass transition temperature T_g, i.e. the temperature of interest, is around 1450 K. For the Lennard–Jones mixtures one can

come somewhat closer to the glass transition temperature, namely almost $T/T_{\rm g} \approx 1.3$. But even for this system it is not yet possible to simulate below T_c, and on the scale of the viscosity the 10 orders of magnitude from $\eta \approx 10^3$ Poise to $\eta(T = T_{\rm g}) = 10^{13}$ Poise cannot yet be explored[18].

In order to learn something about the behavior at and below $T_{\rm g}$, one needs to resort to even simpler but rather abstract models of the spin glass type. However, the standard spin glasses (Fig. 2) are not good models of the structural glass transition: they show a gradual onset of glass behavior, i.e. for $T < T_{\rm g}$ the spin glass order parameter $q_{\rm EA} = [\langle S_i \rangle^2]_{\rm av}$ increases gradually, according to a power law with a critical exponent β, $q_{\rm EA} \propto (1 - T/T_{\rm g})^{\beta}$[2,19]. From Fig. 5, however, it is clear that the "nonergodicity parameter" — which plays the role of an order parameter of the glass transition — becomes nonzero via a discontinuous jump.

However, such a case can be realized with spin glass models, too, for instance, the 10–state mean–field Potts glass. In this model, each spin S_i can be in one of 10 discrete states, and the energy J_{ij} is only nonzero if a pair of spins (S_i, S_j) is in the same state, while otherwise $J_{ij} \equiv 0$. A mean–field model is defined by introducing such an energy function between any pair of spins in the system, independent of their distance. The model shows a glass transition by choosing a Gaussian distribution of interactions J_{ij} (with negative mean). Interestingly, this model shows two transitions in the thermodynamic limit (number of spins $N \to \infty$): at T_D a dynamical transition occurs from ergodic to non–ergodic behavior, of the type described by MCT[20]. The time–displaced spin–spin autocorrelation function shows the same behavior as $\Phi_q(t)$ in Fig. 5! In addition, there is a static transition at $T_0 < T_D$, where $q_{\rm EA}$ jumps discontinuously from zero to a nonzero value, and the (configurational) entropy has a kink (if one would extrapolate the entropy of the high temperature phase to $T < T_0$, one indeed would also find a "Kauzmann temperature" T_K below which the entropy would become negative, but this has no physical significance, the "entropy catastrophe" at T_K is preempted by the static transition at $T > T_K$).

A Monte Carlo study[21,23] of this model is of interest, because computer simulations always deal with finite systems, where phase transitions are shifted in temperature and smeared out (i.e., critical singularities and jump discontinuities cannot straightforwardly be observed, rather one always observes a gradual behavior). Fig. 7 shows the relaxation time and Fig. 8 the entropy of this model, both plotted versus inverse temperature. In the case of the entropy, exact results for $N \to \infty$ are available[22] and included for comparison. Indeed this model for finite N exhibits a gradual crossover from a power law divergence of the relaxation time (for $T > T_D$) to an exponential divergence (of Arrhenius type) for $T < T_D$. The activation energy E_A increases with increasing N. (For this mean–field model the barriers between the different valleys in configuration space have a finite height only if N is finite.) Both static and dynamic properties of this model exhibit considerable finite size effects, which are still understood only partially. At this point, we do not yet know whether analogous size effects are to be expected for the more realistic models of the structural glass transition, considered in the previous sections.

5 Concluding Remarks

In this report, we have demonstrated that large scale computer simulations can indeed give a lot of insight into the challenging problem of glasses and the glass transition, even though

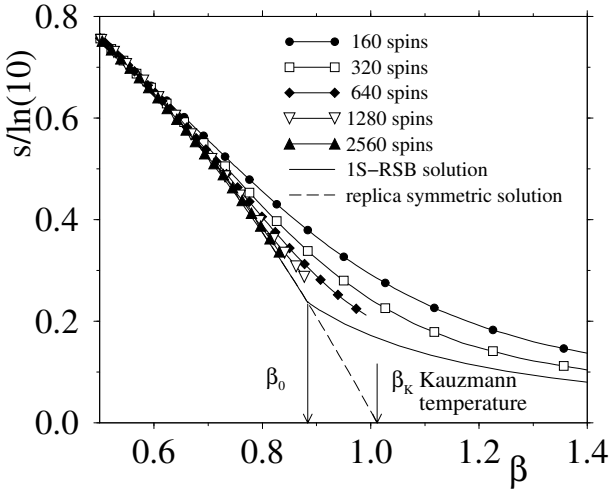

Figure 8. Entropy per spin for the $p = 10$ state Potts glass with random mean field interaction, and normalized by its high temperature value, plotted vs. inverse temperature $\beta = 1/(k_B T)$ ($\beta_0 = 1/(k_B T_0)$, $\beta_K = 1/(k_B T_K)$). Different system sizes are shown (curves with symbols). The dashed and solid curves are the replica–symmetric and one–step replica symmetry broken (1S–RSB) solutions[22], respectively. From Brangian *et al.*[21]

not all questions of interest can be answered yet. While chemically realistic models elucidate the understanding of particular experimental data and complement them in certain directions (e.g. SiO_2 at $T \geq 2750$ K, where no measurements can be done), there is still a considerable gap between the range of time scales accessible in experiment and in the simulations. While techniques such as "parallel tempering"[23] can help to win about a decade in time or so, Fig. 1 demonstrates that there is need for more fundamental ideas to bridge this gap in the time–scale.

A major achievement of the simulation of the binary Lennard–Jones mixture is the extensive test provided of the mode coupling theory. The existing experiments are obscured by many complicating details, because additional molecular degrees of freedom provide additional structure in the relaxation and response functions, and are much more difficult to interpret. In addition, the simulations have begun to yield insight on the fascinating interplay of confinement and surface effects on the glass transition.

Although the simulation of spin glass models is an active topic since 25 years, our recent study[21] reveals that there are still many open problems, and in particular finite size effects are not yet well understood. Since in many areas of computer simulations the understanding of finite size effects has been crucial, clearly more work in this field is still necessary.

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18. For SiO_2 one finds $\eta(T_c) \approx 10$ Poise and $T_c = 3330$ K and thus also temperatures below T_c to some extent are accessible[1]. However, this case is somewhat pathological, since $T_c \approx 1.6 T_m$, very different from the situation sketched in Fig. 5.
19. Here S_i is the value of spin number i and the notation $[...]_{\rm av}$ stands for averaging over the quenched disorder, e.g. the configurations where the nonmagnetic atoms sit in the $Eu_xSr_{1-x}S$ crystal (Fig. 2). Such a quenched disorder, present already at high temperatures, cannot be identified for the structural glass transition at all.
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